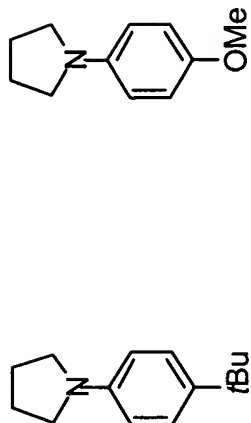
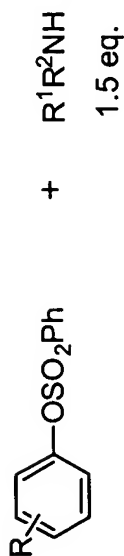
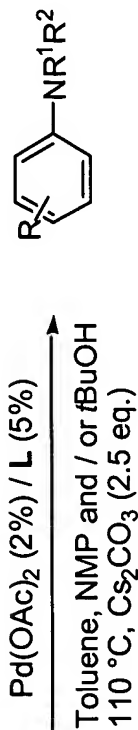
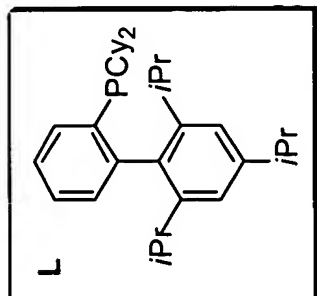
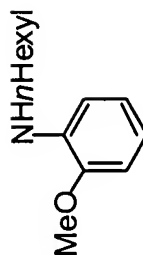


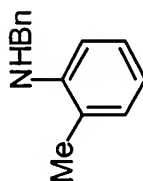
Pd-Catalyzed C-N Bond Formation on Benzenesulfonates



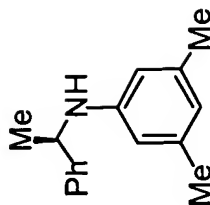
98% yield
8% L was used



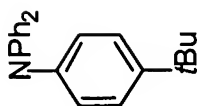
87% yield



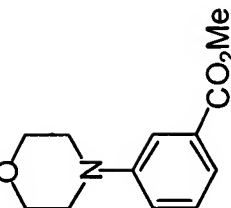
88% yield



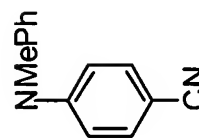
92% yield, rxn temp. was 90°C
ee of starting material: 96%
ee of product: 94%



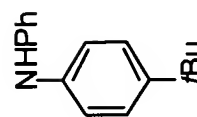
92% yield



> 99% yield
From tosylate



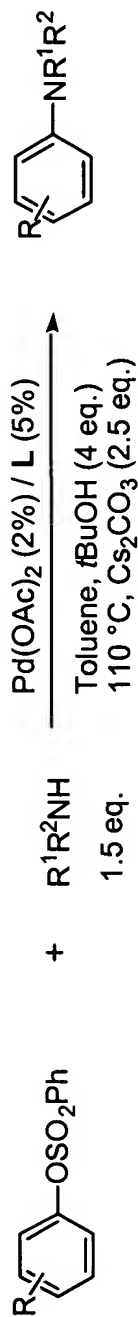
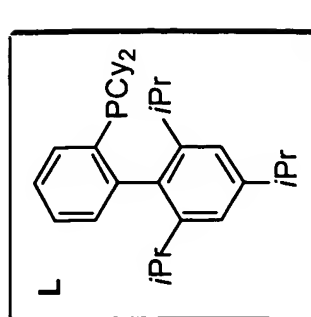
91% yield
From tosylate,
 K_3PO_4 was the base



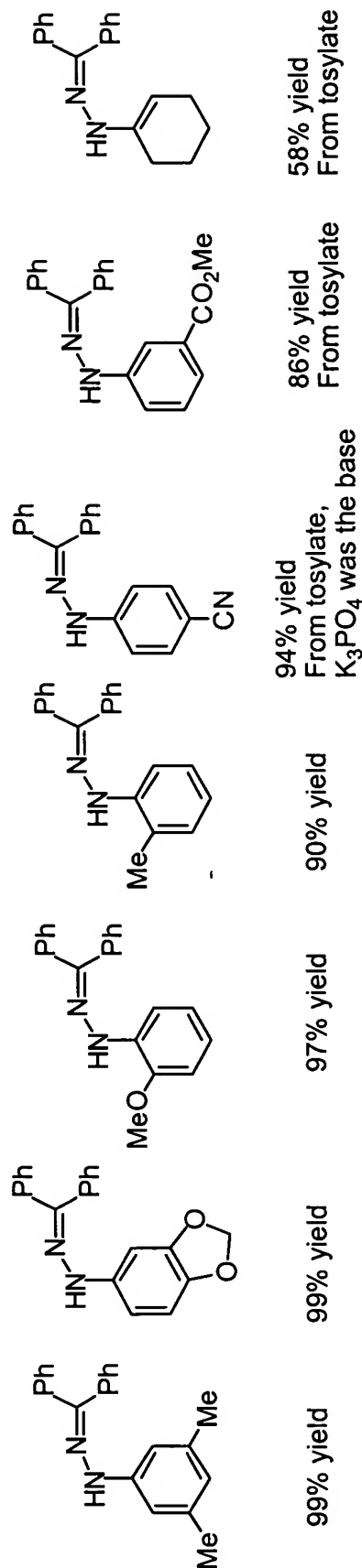
95% yield

Figure 2

Pd-Catalyzed C-N Bond Formation on Benzenesulfonates

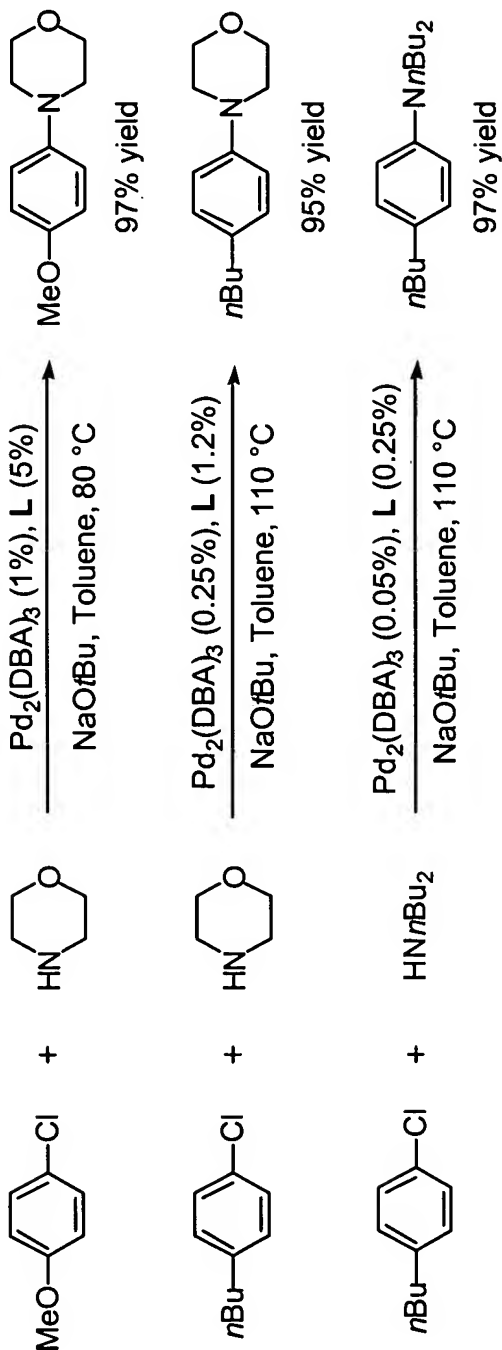


• Benzophenone hydrazone



Pd /Ar₃P on Aryl Chlorides in Cross Coupling Reactions

• Amination



• Suzuki reaction

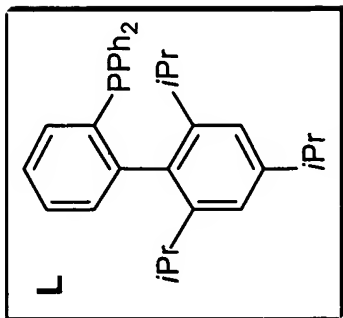
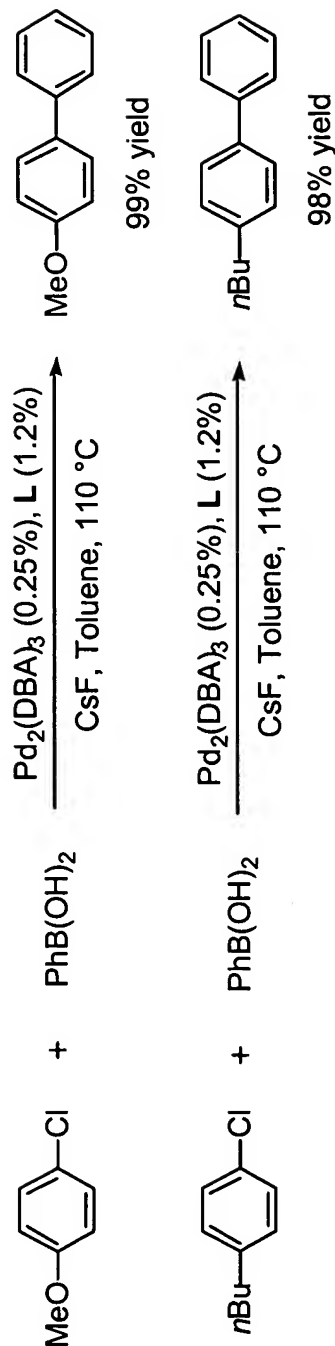


Figure 4

Pd/Ar₃P on Aryl Chlorides in Cross Coupling Reactions

• ***Arylation on ketone and esters***

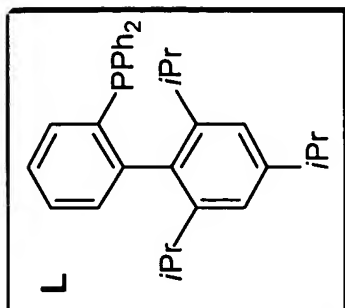
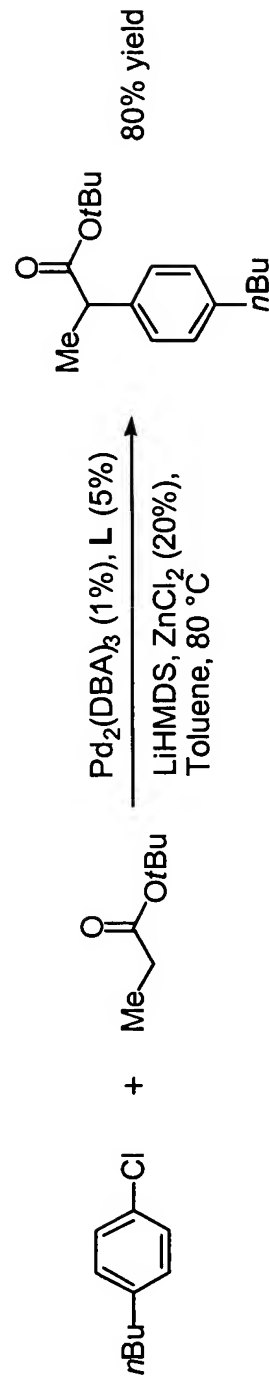
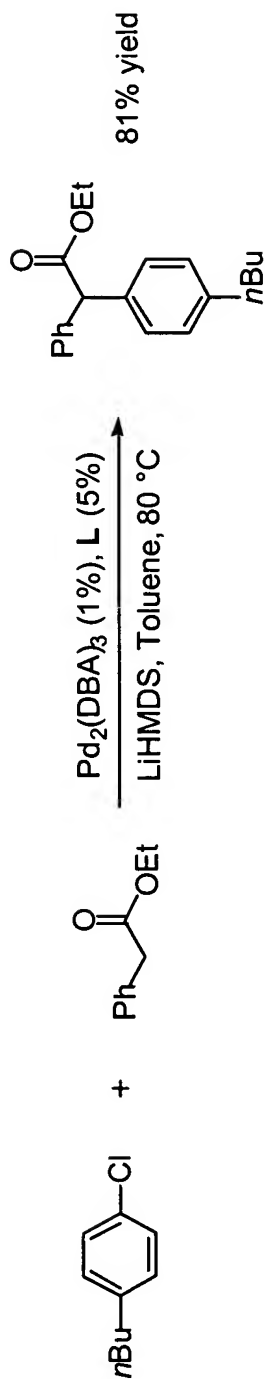
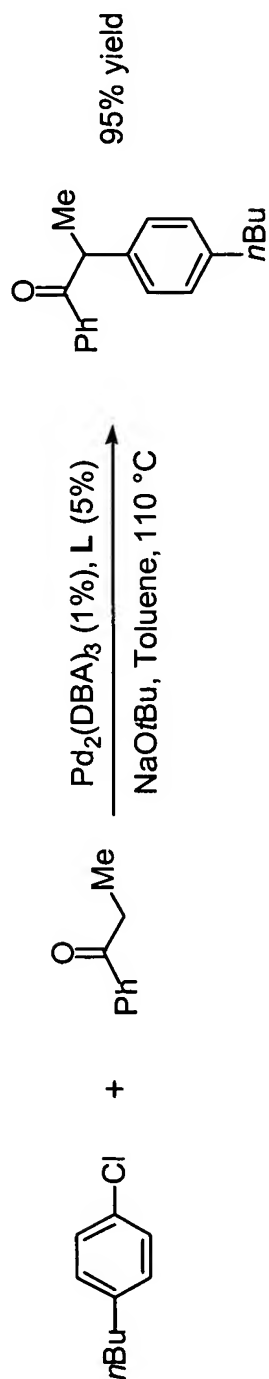


Figure 5

Ligand Comparison

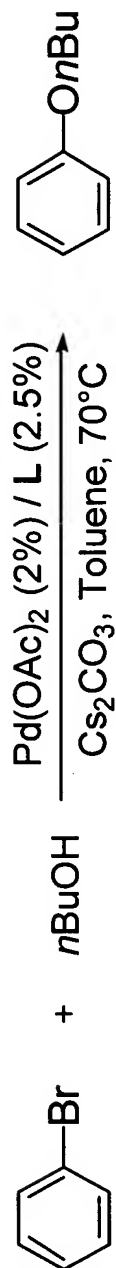


Figure 6

•The presence of a substituent in the 6-position of the phosphine-containing ring is beneficial.

L	GC yield of desired product				
	97%		44%		26%
	29%		3%		66%
			65%		85%



Figure 7

Ligand Comparison

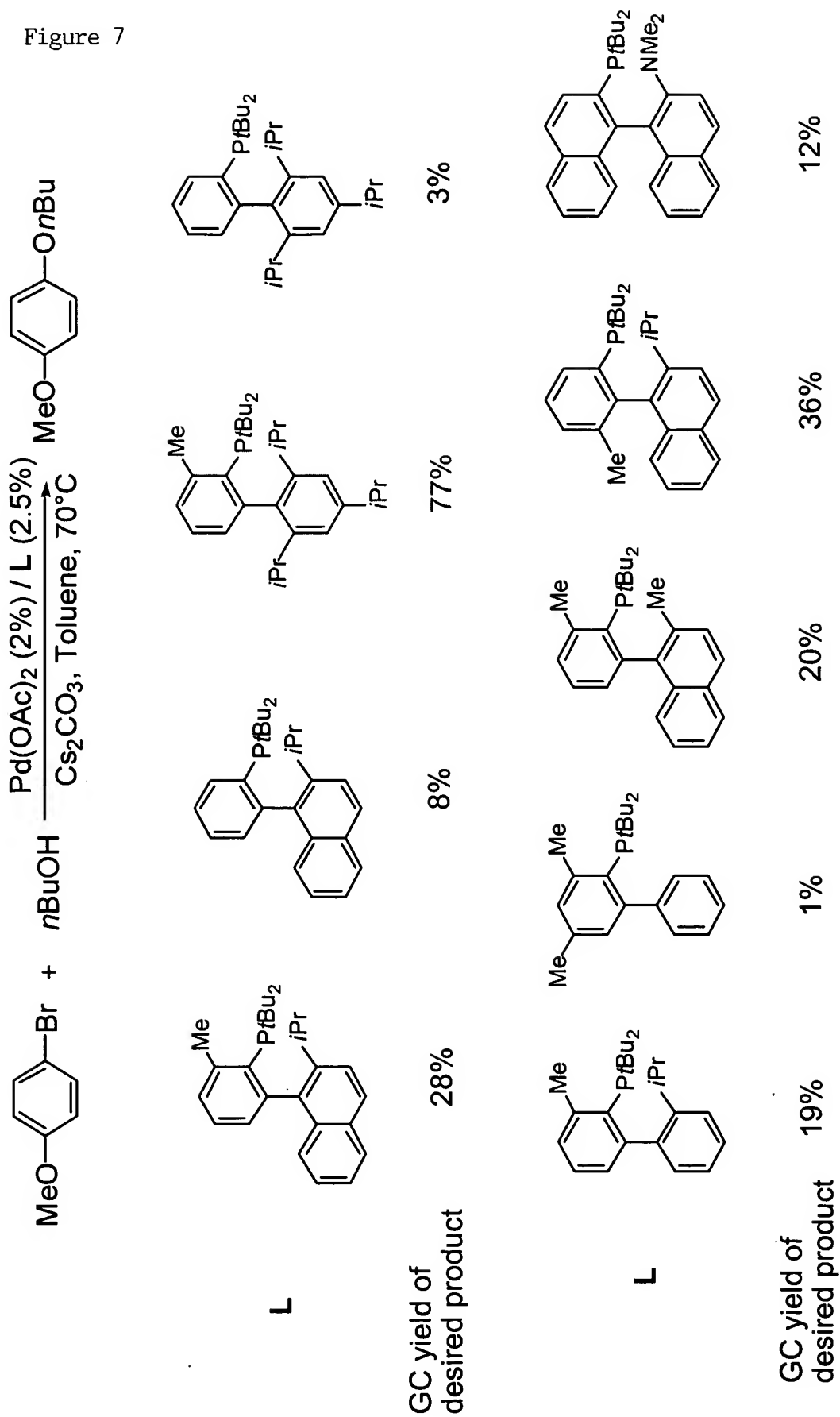
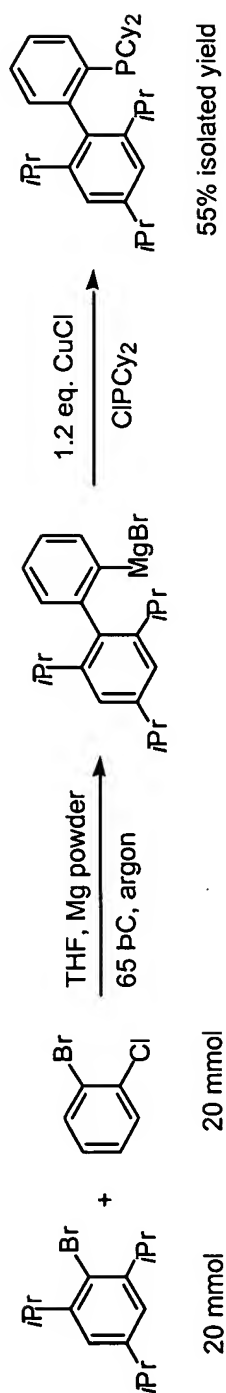


Figure 8

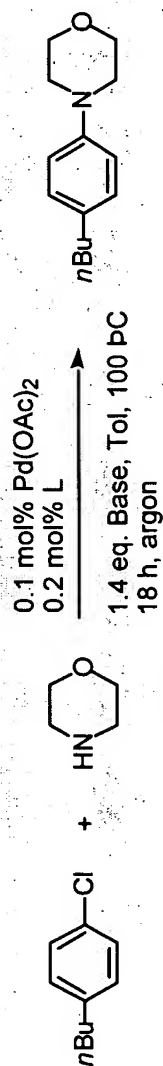
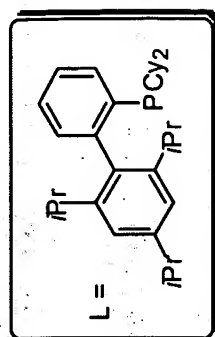
Preparation of biaryl phosphine ligand



Pd-catalyzed Amination of Aryl Chloride: Base Effect



0.1 mol% Pd, 100 pC



1.0 mmol

1.5 mmol

Figure 9

entry	base	% conv. of ArCl	% GC yield ^a
1	K ₃ PO ₄	1	0
2	K ₃ PO ₄ • H ₂ O	2	0
3	K ₂ CO ₃	2	0
4	CS ₂ CO ₃	8	3
5	NaOtBu	98	87 ^b
6	KOAc	2	0
7	KOH	100	98 (98% iso. yield)

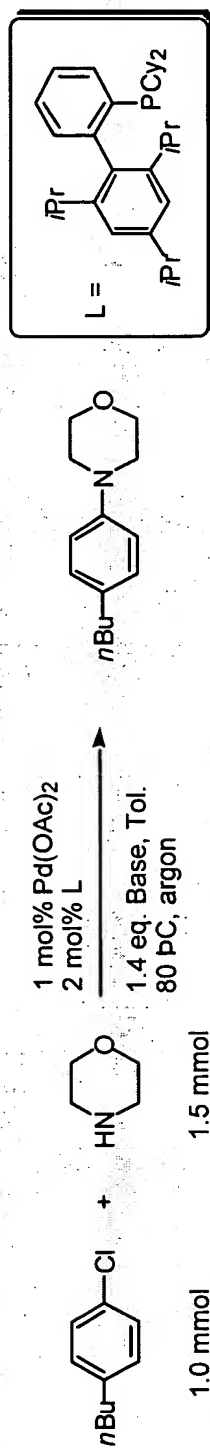
^a Dodecane was used as the internal standard.

^b 2% reduction product was observed.

Pd-catalyzed Amination of Aryl Chloride: Base Effect

Figure 10

1 mol% Pd, 80 °C

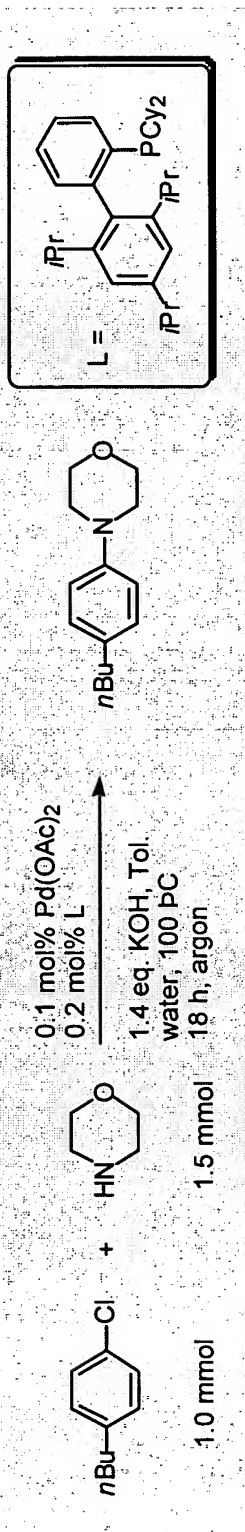


entry	base	2 hours		18 hours	
		% conv. of ArCl	% GC yield ^a	% conv. of ArCl	% GC yield ^a
1	K ₃ PO ₄	11	11	65	63
2	K ₃ PO ₄ • H ₂ O	23	23	72	69
3	K ₂ CO ₃	1	1	39	38
4	Cs ₂ CO ₃	18	18	97	93
5	NaOt-Bu	>99	>99	/	/
6	KOH	99	99	/	/
7	NaOH	72	72	>99	96

^a Dodecane was used as the internal standard.



Pd-catalyzed Amination of Aryl Chloride: Water Effect



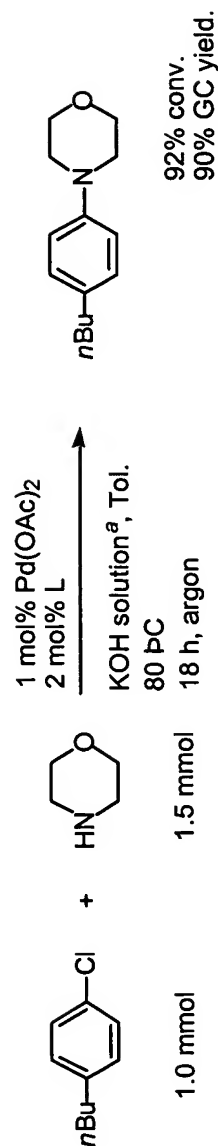
entry	mol% of water (vol)	% conv. of ArCl	% GC yield ^a
1	0 (0 µL) ^b	100	>99
2	50 (9 µL) ^b	92	88
3	100 (18 µL) ^b	100	98
4	200 (36 µL) ^b	78	74
5	500 (90 µL) ^c	1	1

^a Dodecane was used as the internal standard.

^b KOH suspension was observed.

^c Clear solution was observed.

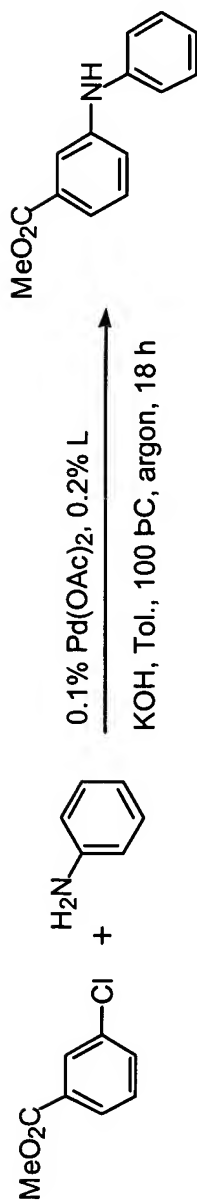
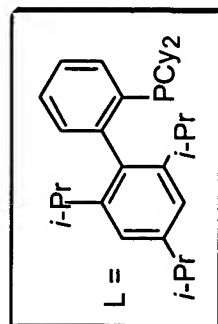
aq. KOH solution:



^a 0.1 mL of 14 M KOH solution was added.

Figure 11

Preliminary Substrate scope using KOH base with 0.1% Pd



Entry	Addition of water	% Conv.	% GC yield
1	0	100	18
2	1 eq. (18μL)	100	76 (iso)

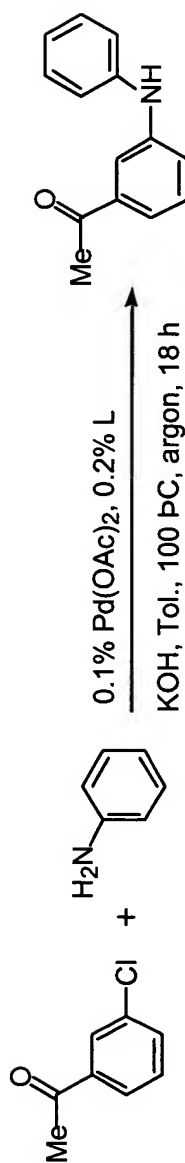
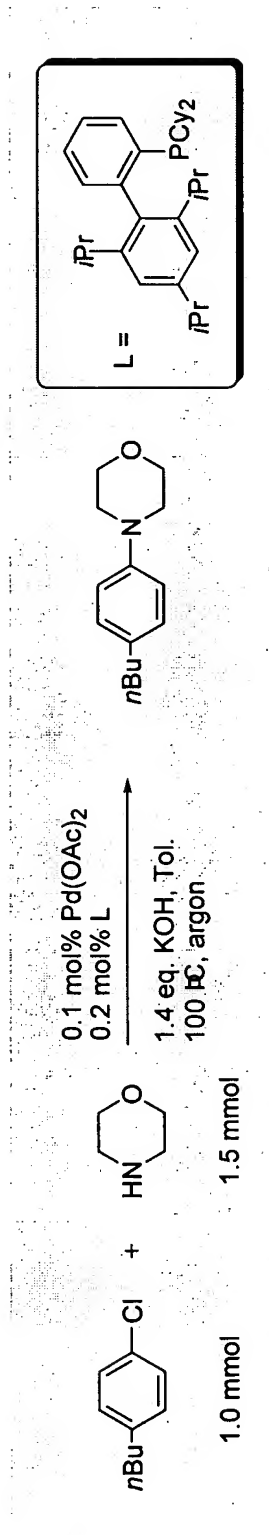


Figure 12

Entry	Addition of water	% Conv.	% uncorrected GC yield
1	0	100	73 (88 iso.)
2	1 eq. (18μL)	100	73

Pd-catalyzed Amination of Aryl Chloride: Reaction Time



entry	Time/h	% GC yield ^a
1	1	23
2	2	48
3	3	78
4	5	>99

^a Dodecane was used as the internal standard.

Figure 13